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Bull. Korean Chem. Soc. **2013**, Vol. 34, No. 2 689
http://dx.doi.org/10.5012/bkcs.2013.34.2.689

E-beam Mediated Ligand Dissociation of Alkyne-Dicobaltcarbonyl Complexes as Potential Photochemical Alkyne Precursor

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Received November 22, 2012, Accepted December 27, 2012

Key Words : Alkyne, Cobalt-complex, Fragmentation, E-beam

Arrayed alkyne group on a solid surface have been of interest for the attachment of diverse agents useful in electronic device coating, fluorescence nanopatterning, and surface reforming.[1] For example, Huisgen reaction of alkynes with organic azides on a surface has been reported to connecting DNA, enzyme and fluorophores on the solid surface.[2-6] The selective immobilization of alkynes on a surface could be progressed by covalent bonding with the arrayed alkyhalide or vinyl halide *via* Sonogashira reaction[7] or by selective thermal degradation of Alkene-SO_2(diarylthiiren-1,1-dioxide).[8] In practice, however, these methods have limitations for the application into surface modification because of relatively vigorous reaction conditions or synthetic difficulty in the precursor supply and requiring of metal catalyst might be interfering with solid surface such as gold and silicone. As an alternate method for selective alkyne generation on the surface, photochemical transformations of furoxane have been reported.[9] Photochemical conversion of furoxane to alkyne on the surface does not require either solvent or catalyst. In a continuation effort to provide efficient alkyne precursors, we synthesized alkyne-cobalt-CO complexes (**1-5**) and analyzed electron beam (e-beam) mediated ligand dissociation in gas phase using MS spectrometer. The complex includes alkynes containing aldehyde and chlorine ligands since those groups could play a role of immobilizing anchor onto gold or silica surface.[9d,10] The ligands, CO and phosphine of cobalt complexes underwent dissociations by e-beam irradiation in gas phase to lead conversion of complexes to alkynes.

The alkyne-cobalt complexes (**1-5**) were prepared from the corresponding alkynes by reacting with cobalt octacarbonyl (Co_2CO_8) followed by ligand exchange with diphenylphosphinomethane (dppm) as reported procedures with minor modification.[11,12] The solution of 5-chloro-1-pentyne (5.13 g, 50 mmol) and dicobalt octacarbonyl (18.81 g, 55 mmol) in toluene (30 ml) was stirred at room temperature for 1 h under N_2 charge for 1h. When the evolution of CO was ceased, solvent was evaporated then the residue was purified with column chromatography (SiO_2, 5% Ethyl acetate/Hexane) to give reddish brown liquid **2** (18 g, 93%).[13] For the synthesis of dppm-cobalt complex, the solution of hexacarbonylcobalt complex **2** (5 g, 12.9 mmol) and dppm (7.3 g, 19.1 mmol) in toluene (30 mL) was stirred at 60 °C for 12 hours. The reaction mixture was concentrated, then purified with column chromatography (SiO_2, EA:Hex = 1:10) to give dppm-cobalt complex **4** as dark brown liquid (6.2 g, 67%).[14] Other complexes **1**, **3** and **5** were also prepared with similar procedures and all the complex's structures were confirmed by the spectroscopic data from IR spectrophotometer (Shimazu, prestige-21), NMR (Varian, Gemini 200 MHz) and mass spectrometer (Micromass Inc, Autospec, at Korea Research Institute of Chemical Technology).[13-15]

The fragmentation of cobalt complexes **1-5** was processed upon 20 eV e-beam at 200 °C in gas phase and the data are listed in Table 1. Mass spectra of hexacarbonyl complexes **2**, **3** and dppm-complexes **4**, **5** are shown in Figures 1 and 2, respectively. The representative fragments are assigned as M+ (molecular ion), M-nCO (CO ligand dissociation), M-dppm (dppm ligand dissociation) and parent alkyne (YN, M-2Co-ligand) as in Scheme 1.

Hexacarbonyl complex **1-3** were fragmented to give six M-nCO peaks *via* CO ligand dissociation. Each M-nCO peaks appeared with *m/z* = 28 difference in 25-100% relative intensity as shown in Figure 2. In case of complex **3**, M-5CO (*m/z* = 276) peak was shown as base peak with other characteristic fragmentation intermediates including Co_2 (*m/z* = 118, 49%), YN (*m/z* = 130, 40%) and YN+Co (*m/z* = 189, 13%) as in Figure 2(a). The YN peaks of hexacarbonyl complexes **1-3** were appeared depending with the structure of cobalt complex. With aryl (**3**) or diaryl (**1**), YN peak intensity was recorded in 32-40%. Meanwhile, YN peak was not observed in case of alkyl complexes **2** and **4**.

Either M-5CO or M-6CO fragment appeared as base peak from hexacarbonyl complexes suggesting that the CO dis-

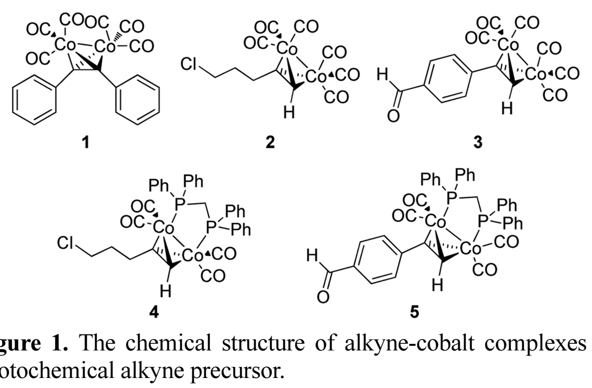


Figure 1. The chemical structure of alkyne-cobalt complexes as photochemical alkyne precursor.

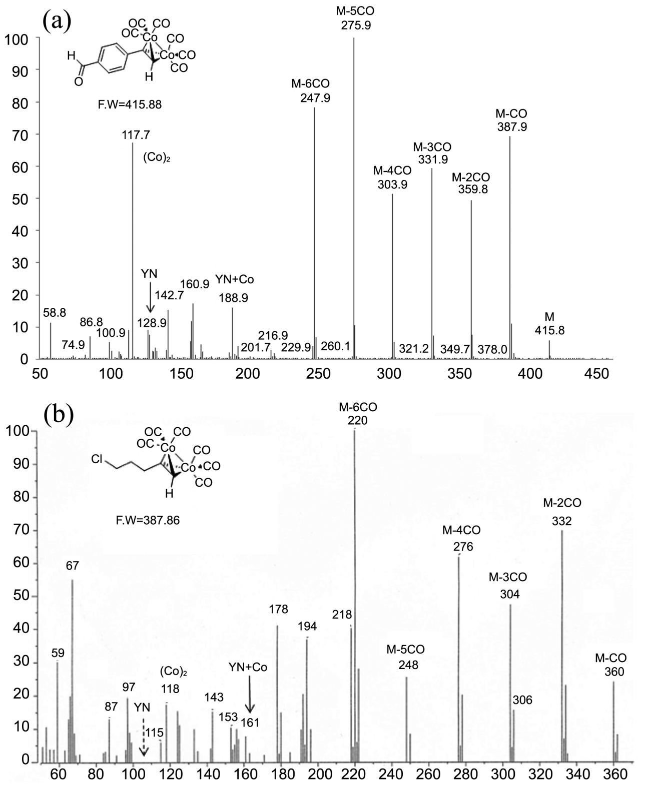


Figure 2. Mass spectra of hexacarbonyl cobalt complex **3**(a) and **2**(b). YN; parent alkyne, M-nCO; dissociation of nCO.

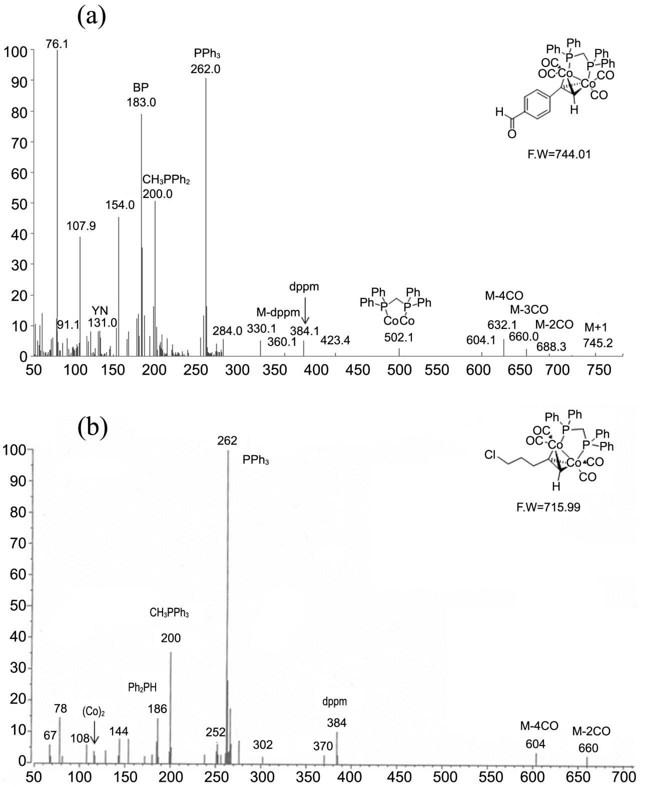


Figure 3. Mass spectra of dppm-cobalt complex **5**(a) and **4**(b). YN; parent alkyne, BP; dehydride of 5*H*-benzo[*b*]phosphindole.[18]

sociation was resulted as one of main fragmentation processes upon e-beam irradiation as like reported photochemical ligand dissociation of cobaltcarbonyl complex in solution.[16,17] M-5CO peak for aryl complex **1** and **3**, and M-6CO (*m/z* = 220) peak for alkyl complex **2** were shown with the highest intensity. The relative stability between M-5CO and M-6CO intermediates, however, is not known requiring further explore. It is interesting that mono-cobalt intermediate, YN+Co peak was observed from aryl-complex **1** and **3**, but that is not shown in case of alkyl-complex **2** as in Figure 2.

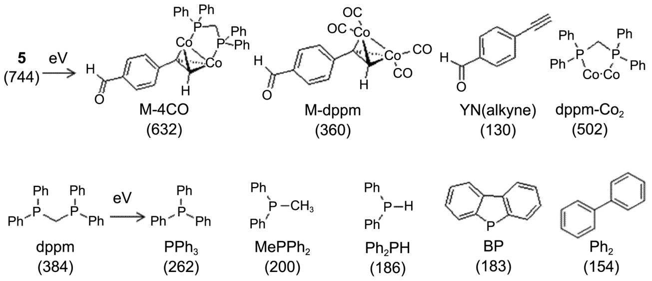
With alkyl substituent, neither molecular ion (*m/z* = 388) nor YN peak (*m/z* = 102) was shown in electron-impacted MS of alkyl complex **2** as in Figure 2(b). The molecular ion peak of complex **2**, however, was detected in FAB mass spectrum. It was assumed that ionized chloropentyne or its cobalt complex was not tolerated to give M+ and alkyne peaks in EI-MS.

In case of dppm-cobalt **4** and **5**, M-nCO (n = 1-4) peaks are also clearly observed by the corresponding CO ligand dissociation likewise in case hexacarbonyl complexes **1-3**. Interestingly, however, dppm ligand dissociation and its degradation were observed as the most abundant fragmentation as in Figure 3. The peaks for M-dppm (*m/z* = 360), Ph_3P (*m/z* = 262), Ph_2PCH_3 (*m/z* = 200) and Ph_2PH (*m/z* = 186) and phosphindole-dehydride[18] (*m/z* = 183) are assigned as possible dppm-derived intermediates in Figure 3. Those peak assignments was confirmed using the EI-mass spectrum of dppm itself.[19] In both case of dppm-complex **4** and **5**, Ph_3P (*m/z* = 262) intermediate was appeared as base peak. The dissociation and subsequent fragmentation of dppm ligand are proposed for P-C bond formation leading diverse dppm-derived intermediates including Ph_3P, Me-PPh_2, Ph_2PH and phosphindole.[18] In case of aryl-dppm complex **5**, alkyne (*m/z* = 130) peak was detected in 8.7%. Meanwhile, M+ and YN (*m/z* = 102) peaks of alkyl-dppm cobalt **4** were not shown as like in alkylhexacarbonyl complex **2**, presumably

Table 1. Relative intensities of the intermediates from alkyne-cobalt complexes **1**-**5** fragmented by 20 eV e-beam irradiation.

	M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	M-6CO	YN	YN+Co	Co_2 (118)	M-dppm	Dppm (384)	Ph_3P (262)	Ph_2PCH_3 (200)
1 (BisPh)	2.5	26.7	24.2	40.0	60.0	100.0	56.7	31.7	25.8	0.8	–	–	–	–
2 (Alkyl)	a	23.7	69.7	47.4	61.8	25.7	100.0	a	7.9	17.1	–	–	–	–
3 (Benz)	4.1	45.3	30.2	33.7	40.7	100.0	88.4	39.5	12.8	48.8	–	–	–	–
4 (Alkyl-P)	a	a	2.6	a	3.9	–	–	a	a	3.9	a (332)	10.5	100.0	35.5
5 (Benz-P)	1.3	0.3	1.2	3.0	6.0	–	–	8.7	a	5.4	0.5 (360)	5.4	100.0	87.2

Parenthesis are *m/z* values; (a), not observed; (–), not available; YN, parent alkyne.



Scheme 1. Proposed intermediates from alkyne-cobalt complex **5** by e-beam mediated fragmentation.

due to instability of chloropentyne intermediate upon e-beam irradiation.

In complex **5**, the intensities of M-nCO peaks (1-6%) were higher than M-dppm peak (*m/z* = 360, 1.3%) which was derived from dppm dissociation. In addition, the appearance of dppm+Co_2 peak (*m/z* = 502) suggested that dissociation of CO ligand of alkyne-cobalt complex seems more facile than dppm liberation upon e-beam irradiation. Also, in a related photolysis of carbonylphosphinocobalt complex in solution, CO dissociation is preferred over the dissociation of phosphine ligand.[16] These observations may be unusual to the prediction that the longer cobalt-phosphine bond (~2.23 Å) should give facile dissociation than short cobalt-CO (~1.78 Å) bond.[20] Nonetheless, the relative dissociation tendency of the ligands between CO and dppm, in gas phase should be remained for further discussion.

In summary, the alkyne-cobalt complexes **1-5** were synthesized and their e-beam mediated fragmentation was processed in gas phase. The ligand dissociation from cobalt complexes resulted in alkyne formation. In case of arylalkyne complex **1**, **3** and **5**, the more alkyne formation was observed than in case of alkylalkyne-cobalt complex **2** and **4**. These results suggested us that aryl-substituted alkyne-cobalt complex could be a potential alkyne precursor on a solid surface *via* photochemical ligand dissociation.

Acknowledgments. This work was supported by a National Research Foundation of Korea Grant funded by the Korean Government (2010-2011).

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14. Analytical data of cobalt-dppm complexes: (4) ^{1}H-NMR δ ($CDCl_3$, ppm); 6.0 (s, 1H, CH-Co), 3.6-3.7 (t, 2H, CH_2-Cl), 3.0-3.1 (t, 2H, CH_2), 2.0-2.2 (m, 2H, CH_2); MS (FAB) *m/z*; 716 (M^+, 2), 660 (M-2CO, 40), 604 (M-4CO, 100), 502 (Co_2-dppm, 16). (5) ^{1}H-NMR δ ($CDCl_3$, ppm); 10.1-10.2 (s, 1H, CHO), 7.7-7.9 (m, 4H, Ar-H), 7.2-7.5 (m, 20H, Ar-H), 5.8-5.9 (m, 1H, C-H), 3.5-3.7 (m, 1H, CH_2), 3.0-3.3 (m, 1H, CH_2).
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